IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of) (2)	
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Igor Igorevitch Diakonov ,) 4	
Alexander Vladimirovitch Zotov)	
Igor Nikolaevitch Solodov)	
Evgenii Grigorevitch Osadchii, and) .	
Alexander D. Khoteev)	,
09/849-059) 1747	
Serial Nº: To be Assigned) Group Art Unit:	
Filed: May 4, 2001	7005	
For: POTENTIOMETRIC SENSOR FOR WELLBORE APPLICATIONS) File: 57.0386	

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uth A. Schreiber

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SUBMISSION OF PRIORITY DOCUMENT

Assistant Commissioner for Patents

Washington, D.C. 20231

Sir:

Attached hereto is United Kingdom Patent Application No 0011965.1, filed 18 May 2000, for the above-captioned application. Priority is claimed under 35 U.S.C. §119 and 37 CFR §1.55.

Respectfully submitted,

William B. Batzer

Registration N° 37,088

Schlumberger-Doll Research Old Quarry Road Ridgefield, Connecticut 06877-4108 (203) 431-5506

Date: May 4, 2001







I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation and Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein together with the Statement of inventorship and of right to grant of a Patent (Form 7/77), which was subsequently filed.

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The Patent Office

Cardiff R ad Newport South Wales NP9 1RH

-

1. Your reference

57.0386 GB ND

2. Patent application number (The Patent Office will fill in this part)

0011965.1

18 MAY 2000

 Full name, address and postcode of the or of each applicant (underline all surnames)

Patents ADP number (If you know It)

Schlumberger Holdings Limited

PO Box 71 Craigmuir Chambers Road Town

Tortola

7236326001

If the applicant is a corporate body, give the country/state of its incorporation

British Virgin Islands

4. Title of the invention

Potentiometric sensor for wellbore applications

5. Name of your agent (If you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Akram Karim MIRZA Schlumberger Cambridge Research Limited High Cross Madingley Road Cambridge CB3 OEL

6974299001

Patents ADP number (if you know it)

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (If you know It) the or each application number

Country

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 Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer Yes' 1f:

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Continuation sheets of this form

Description 16

Claim (s) Z

Abstract /

Drawing (s)



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Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

> Any other documents (please specify)

> > I/We request the grant of a patent on the basis of this application.

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12. Name and daytime telephone number of person to contact in the United Kingdom

Akram MIRZA, 01223 325268

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Statement of invent rship and f right to grant of a patent

THE PATENT CHACE A 2.7 JULY 2009

The Patent Office

Cardiff Road Newport South Wales NP9 1RH

1. Your reference

57.0386 GB NP

2. Patent application number (If you know It)

0011965.1

3. Full name of the or of each applicant

Schlumberger Holdings Limited

4. Title of the invention

Potentiometric sensor for wellbore applications

- 5. State how the applicant (s) derived the right from the inventor (s) to be granted a patent The applicant derived the right to be granted a patent by agreement with the Employer(s) of the Inventor(s) and/or agreement with the Inventor(s).
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 (see note (c))

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26 June 2000

8. Name and daytime telephone number of person to contact in the United Kingdom

William L. WANG, 01223 325268

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Statement of inventorship and of right to grant of a patent

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Signature

26 June 2000

8. Name and daytime telephone number of person to contact in the United Kingdom William L. WANG,

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Enter the full names, addresses and postcodes of the inventors in the boxes and underline the surnames

Igor Igorevitch DIAKONOV 36 St. Stephen's Place Cambridge CB3 OJE United Kingdom

Patents ADP number (if you know it): 7-127 270001

Alexander Vladimirovitch ZOTOV Flat 78, Building 38/1 Znamenskaya Street 107 392, Moscow Russia

Patents ADP number (if you know it): 792729600

Igor Nikolaevitch SOLODOV Flat 209, Building 13/2 Svobodi Street 123 362 Moscow Russia

Reminder

Have you signed the form?

Patents ADP number (If you know it): 7 ? 27 512CC

Enter the full names, addresses and postcodes of the inventors in the boxes and underline the surnames	Evgenii Grigorevitch OSADCHII 4A, Apartment 31 Centralnaya Street Chernogolovka 142 432 Moscow RUSSIA
	Patents ADP number (if you know it): 7727355CC
	Patents ADP number (if you know it):
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DUPLICATE

- 1 -

Potentiometric Sensor for Wellbore Applications

The invention relates to a chemical sensor tool for use in downhole analyzing of fluids produced from subterranean formations. More specifically it relates to a potentiometric sensor for downhole pH and ion content analysis of effluents produced from subterranean formation

BACKGROUND OF THE INVENTION

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- Analyzing samples representative of downhole fluids is an important aspect of determining the quality and economic value of a hydrocarbon formation.
- 15 Present day operations obtain an analysis of downhole fluids usually through wireline logging using a formation tester such as the MDT ™ tool of Schlumberger Oilfield Services. However, more recently, it was suggested to analyze downhole fluids either through sensors permanently or quasi-permanently
- 20 installed in a wellbore or as through sensor mounted on the drillstring. The latter method, if successful implemented, has the advantage of obtaining data while drilling, whereas the former installation could be part of a control system for wellbores and hydrocarbon production, therefrom.

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To obtain an albeit crude estimate of the composition of downhole fluids, the MDT tools uses an optical probe to estimate the amount of hydrocarbons in the samples collected from the formation. Other sensors use resistivity measurements to discern 30 various components of the formations fluids.

Particularly, knowledge of downhole formation (produced) water chemistry is needed to save costs and increase production at all stages of oil and gas exploration and production. The following 35 applications are of interest:

- -Prediction and assessment of mineral scale and corrosion;
- -Strategy for downhole oil/water separation and water reinjection;
- 5 -Understanding of reservoir compartmentalization / flow units;
 - -Characterization of water break-through;
 - Derivation of Rw.

Some chemical species dissolved in water (like, for example, Cland Nat) do not change their concentration when removed to the 10 surface either as a part of a flow through a well, or as a sample taken downhole. Consequently information about their quantities may be obtained from downhole samples and in some cases surface samples of a flow. However, some chemical species, such as H^+ (pH = -log[concentration of H^+]) CO_2 , H_2S and water 15 parameters, such as ORP (redox potential or Eh), do change significantly while trip to the surface. This change occurs mainly due to a huge difference in temperature and pressure between downhole and surface environment. In case of sampling, 20 this change may also happen due to degassing of a sample (seal failure), mineral precipitation in a sampling bottle, and (especially in case of H_2S) - a chemical reaction with the sampling chamber. It should be stressed that pH, H_2S , CO_2 , and ORP are among the most critical parameters for corrosion and scale assessment. Consequently it is of considerable importance 25 to have their downhole values precisely known.

Hence, there is and will continue to be a demand for downhole chemical measurements. However, no downhole chemical

30 measurements actually performed in a oil and gas producing well have been reported so far.

To meet demand for chemical measurements of increasing accuracy, it may appear obvious to adapt chemical analysis tools known from chemical laboratory practice to the hostile environment of

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a subterranean borehole. Such known analysis tools include for example the various types of chromatography, electrochemical and spectral analysis. Particularly, the potentiometric method has been widely used for the measurements of water composition (pH, Eh, H,S, CO, Na⁺, Cl⁻ etc...) both in the laboratory and in the field of ground water quality control. However, so far the environmental conditions within a subterranean wellbore rendered attempts to perform such measurements under real hydrocarbon wellbore condidtion purely theoretical.

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Among the known state of the art in the field of high temperature potentiometric are: Diakonov I.I., Pokrovski G.S., Schott J., Castet S., and Gout R. J.-C. "An experimental and computational study of sodium - aluminum complexing in crustal fluids", in: Geochim. Cosmochim. Acta, 60(1996), 197-211 and Midgley D. "A review of pH measurement at high temperatures", in: Talanta, 37(1990), 8, 767-781.

General downhole measurement tools for oilfield applications are known as such. Examples of such tools are found in the United States Patents Nos. 6,023,340; 5,517,024; and 5,351,532 or in the International Patent Application WO 99/00575. An example of a probe for potentiometric measurements of ground water reservoirs is published as: Solodov, I.N., Velichkin, V.I., Zotov, A.V. et al. "Distribution and Geochemistry of

Contaminated Subsurface Waters in Fissured Volcanogenic Bed Rocks of the Lake Karachai Area, Chelyabinsk, Southern Urals" in: Lawrence Berkeley Laboratory Report 36780/UC-603(1994b), RAC-6, Ca, USA.

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It is therefore an object of the present invention to provide apparatus and methods to perform potentiometric measurements in a subterranean wellbore for hydrocarbon exploration and production.

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SUMMARY OF THE INVENTION

The invention achieves its objects by providing a potentiometric sensor with at least one reference and one measuring electrode

5 having a permanent aqueous contact between measuring and reference electrode. The contact is preferably ensured by discharging the internal solution from the reference electrode directly onto a measuring (ion-sensitive) membrane and protecting the reference junction of the reference electrode

10 with water wet porous material, such as sintered glass.

In a preferred embodiment, the stability of a signal / electrode fouling can be checked by measuring a signal with and without an additional resistance.

A potentiometric technique can be applied for example as part of a production logging tool and open hole formation tester tool (Modular Dynamic Tester, MDT). In the latter case, the technique can provide a downhole real-time water sample validation or downhole pH and H_2S measurements for prediction of mineral scale and corrosion assessment. A new gas sensing combination potentiometric sensor is also proposed for simultaneous detection of H_2S and CO_2 partial pressures in any fluid (oil, gas, water).

These and other features of the invention, preferred embodiments and variants thereof, possible applications and advantages will become appreciated and understood by those skilled in the art from the following detailed description and drawings.

DRAWINGS

FIG. 1 shows a schematic diagram of the main elements of a known potentiometric sensor;

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- FIG. 2 shows details of a reference electrode of a known potentiometric sensor;
- FIG. 3 shows a schematic diagram of a downhole probe with a of a potentiometric sensor;
 - FIG. 4 shows a schematic diagram of the main elements of an example of a potentiometric sensor in accordance with the present invention;
- FIGs. 5A,B illustrate variants of a potentiometric sensor in accordance with the present invention;
- FIG. 6 shows a self-discharging reference electrode for use
 as part of a potentiometric sensor in accordance with
 the present invention;
 - FIG. 7,8 illustrates further variants of discharging electrodes; and
 - FIG. 7 illustrates a further variant of an analyzing tool as part of a permanently installed flow monitoring unit in a wellbore.

MODE(S) FOR CARRYING OUT THE INVENTION

The theory of potentiometry and its application to water measurements at ambient temperatures are well developed. The 30 method is based on the measurement of electromotive force (e.m.f., or E) in a potentiometric cell which consists of measuring and reference electrodes (half-cells).

FIG. 1 shows the general components of a known potentiometric cell. A measuring electrode is inserted into a solution. This

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electrode consists of an internal half element (for example, Ag wire covered by an AgCl salt) in a solution of a fixed pH (for example, 0.1M HCl in some pH electrodes), and an ion-selective membrane (like glass H selective membrane in pH glass electrode). The reference electrode also contains an internal half-element (typically the same AgCl; Ag) inserted in a concentrated KCl (for example 3M) solution / gel saturated with Ag , which diffuses (or flows) through the reference (liquid) junction.

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Details of the reference electrodes are shown in FIG. 2: A reference electrode contains an internal half-element (typically AgCl;Ag) inserted in a concentrated KCl (for example 3M) solution / gel saturated with Ag⁺, which diffuses (or flows)

15 through the reference (liquid) junction, thus maintaining electrical contact. The potential of this electrode is fixed at a constant temperature as chloride ion concentration inside is a constant. It is important that the membrane (RJ) should stay intact (no clogging / fouling) and consequently (b) there should aqueous continuum between measuring and reference electrode.

The ion-selective electrode measures the potential that arises because of the difference in concentrations of a corresponding ion (H⁺ in case of pH) in the internal solution and in the measured solution. This potential is measured against the reference potential on the reference electrode, which is fixed because of a constant composition of a reference solution / gel (see FIG. 2). Electrodes may be separate (separate half cells), and combined into one ("combination electrode").

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The measuring electrode has a special sensitive ion-selective membrane. The membrane potential is related to the activity (concentration) of a given ion in a solution. The reference electrode has a constant potential (see FIG. 2). The measured e.m.f. (E, potential difference) is an overall a function of the

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temperature and the activity of an ith ion, to which the measuring electrode is selective:

[1]
$$E = E^{0} + (k*T)*log(a_{i}),$$

where E is the measured electromotive force (e.m.f.) of the cell (all potentials are in V), a corresponds to the activity of the ith ion and is proportional to its concentration. E0 is the standard potential (at temperature T) corresponding to the E 10 value in a solution with the activity of ith ion equal to one. The term in parenthesis is a so-called Nernstian slope for the plot of E as a function of $log(a_i)$. This slope (or the constant "k") together with the cell (electrode) constant (E^0) is experimentally determined via a calibration procedure using standard solutions with known activities of ith ion. For good quality undamaged electrodes this slope should be very close to the theoretical one, equal to (R*T/F*z), where F is the Faraday constant (23061 cal/mole), R is the gas constant (1.9872 cal/mole K), zi is the charge of ith ion. The schematic design of a potentiometric cell is shown in FIG. 1 above. Note that potentiometric electrodes may be used as separate entities (separate, individual electrodes, or half-cells) or be assembled in a "combination" electrode (like very popular pH combination glass electrode).

In FIG. 3, there are schematically illustrated elements of a known downhole analyzing tool as used by Solodov et al (see background). Potentiometric electrodes are located at the bottom part of the probe and include those for pH, Eh (or ORP), Ca2+ (pCa), Na^{+} (pNa), S^{2-} (pS), NH_{4}^{+} (pNH₄), and reference electrode 30 (RE). H₂S partial pressure may be calculated from pH and pS readings.

In the follow major aspects of the invention are described in 35 detail. These aspects cover three main areas:

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- The adaptation of potentiometric method to measurements in oil/water mixtures including oil-continuous phase
- Use of the method in downhole tools
- 5 Design of a new gas-sensing combination electrode for the simultaneous detection of CO_2 and H_2S partial pressures

A first aspect relates to the adaptation of potentiometric method to measurements in oil/water mixtures including oil10 continuous phase.

Such Potentiometric measurements are feasible under two conditions:

15 Firstly, the membranes (measuring and RJ) should stay intact without clogging or fouling. The second condition is to provide an aqueous continuum between measuring and reference electrode.

It was found that glass and silver sulfide membranes are not
prone to immediate fouling by oil and its components.
Consequently, in this invention devices are used which eliminate fouling or clogging of the reference junction (RJ) of the reference electrode. Simultaneously with eliminating RJ fouling these devices help to establish a stable aqueous contact between measuring and reference electrodes thus allowing stable measurements in oil continuous phase. Some of the proposed devices also decrease fouling of the ion-sensitive membranes of the measuring electrodes.

- All of the above is achieved by using a passive water-wet protection layer on the reference junction. The protection layer is manufactured from special porous water wet materials (for example, a sintered glass frit). When used in combination electrodes with glass/silver sulfide (or similar) membranes
- 35 which are not very prone to fouling, this device enables

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measurements until glass membrane fouling occurs as it does not protect the measuring electrode.

By adding an induced discharge of the reference solution / gel directly onto measuring membrane of the measuring (ion-selective) electrode, a closed electrical circuit is created even in water-in-oil emulsions. This procedure may be applied in conjunction with the use of the above-described water-wet protective cap. In combination, discharge and cap allow measurements in oil continuous phase (maintaining water layer on measuring surface and RJ) and simultaneous membrane cleaning by an induced discharge of reference fluid. This reference fluid may also clean the membrane of the measuring electrode.

- 15 FIG. 4 shows a combination pH electrode consists of pH glass electrode and an enveloping reference electrode. Reference electrode has a protective water-wet cap on the reference junction. The cap is made from sintered glass, This material may or may not itself be saturated with the reference gel. A 20 protective water-wet cap ensures a constant presence of a water continuous layer on the surface of the cap and consequently a closed circuit with the measuring glass pH membrane. KC1 gel / solution either diffuses through the cap, or is pushed through via various means to ensure electrical contact. The water 25 present in water-in-oil emulsion exchanges with the water in a surface layer on top of this sensor. Consequently, the measurement accounts for any change in the effluent passing the sensor (see Fig. 4).
- 30 In FIGs. 5A and 5B there are shown two variants having a separate reference and measuring electrodes. The measuring glass membrane of pH electrode is water-wet. An electrical contact in water-in-oil emulsions is assured via a direct discharge of a reference solution / gel onto a surface of the measuring
 35 membrane. This is achieved either via diffusion (or induced

- 10 -

flow) through a water -wet protective cap (e.g. a sintered glass disc) (FIG. 5A) or through a capillary contact (FIG. 5B). The reference solution / gel may be pushed out from the reference electrode via various means.

Direct discharge of reference solution / gel is achieved via pushing it out of the reference electrode with the help of

- a piston;

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- 10 a load, placed on top of an inflatable chamber filled with reference solution;
 - -a buoyancy system, where a floating chamber is filled with a light gas is placed underneath a flexible chamber filled with the reference solution. Consequently, this floating chamber
- 15 exert a pressure onto a flexible tank with a reference fluid; or variants or combinations thereof.

A self-discharging type reference electrode is shown in FIG. 6. The reference electrode may be filled with aqueous solution

(usually KC1), gel, or solid electrolyte (or it may contain a solid micro-porous matter saturated with an aqueous solution or gel). The induced discharge of the reference electrolyte establishes an aqueous electrical contact with the measuring

electrode. The discharge itself is achieved using a selfcompressing deformable reference electrode (2). A flexible bag
(2) is charged in a stretched state. The bag is then closed by a
gland (3) having a central passage filed with a micro-porous
medium (4). The elastic force compresses the bag and pushes
solution out through the medium (4). In this design, neither the
rate nor time of solution outflow may be controlled.

Further examples of discharge type reference electrodes are shown in FIGs. 7 and 8.

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The electrode of FIG.7 comprises a piston exerting a pressure onto an inner chamber of the reference electrode. The chamber is filled with the reference aqueous solution or gel. The porous water-wet material of the cap ensures an electrical contact to the pH sensing membranes. In operation the piston can be driven by an external motor or hydraulic system.

In the variant of FIG. 8, a gas-filled chamber replaces the piston of FIG. 7. The reference solution is stored in a flexible 10 bag.

The above sensor design can be improved by an internal measurement against a known resistor as shown in FIG. 9. An additional resistance "R" placed between the measuring and 15 reference electrodes will enable a check for electrical contact quality to be carried out. The electrode pair may be regarded as a battery with its internal resistance "r". This internal resistance is caused by electrodes and the measuring solution. The resistance of the glass electrodes is very high (>10 MOhm), 20 whereas the resistance of the pure aqueous solutions (no oil) and the reference electrode (Ag, AgCl) is very small compared to the resistance of the glass electrodes. The resistance of oil may be comparable to that of the glass electrodes. Consequently, when the space between the electrodes fills with oil, the oil 25 forms a fouling film on their surfaces, the overall resistance of a cell increases and the signal changes. Measuring this cell resistance with the help of a reference measurement performed employing an additional resistance "R" indicates the quality of the electrical contact. A condition for a good electrically 30 conductive circuit is a stable, constant voltage drop when the additional resistance is switched on.

A compact potentiometric probe of particular use for a downhole application is shown in FIG. 10. The probe may be placed inside the module body (shown) or inside a sampling bottle. A system of

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valves, flow lines and additional chambers (not shown) ensures the contact of the probe's sensors with the sample effluent. This system may also supply calibration and cleaning solutions downhole.

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In FIGs. 11 - 13 the sensor is shown in various possible downhole applications.

In FIG. 11, there is shown a formation testing apparatus 110 10 held on a wireline 112 within a wellbore 114. The apparatus 110 is a well- known modular dynamic tester (MDT, Mark of Schlumberger) as described in the co-owned U.S. Pat. No. 3,859,851 to Urbanosky U.S. Pat. No. 3,780,575 to Urbanosky and Pat. No. 4,994,671 to Safinya et al., with this known tester 15 being modified by introduction of a potentiometric analyzing tool 116 as described in detail above. The modular dynamics tester comprises body 120 approximately 30m long and containing a main flowline bus or conduit 122. The analysing tool 116 communicates with the flowline 122 via opening 117. In addition 20 to the novel sensor system 116, the testing apparatus comprises an optical fluid analyser 130 within the lower part of the flowline 122. The flow through the flowline 122 is driven by means of a pump 132 located towards the upper end of the flowline 122. Hydraulic arms 134 and counterarms 135 are 25 attached external to the body 120 and carry a sample probe tip 136 for sampling fluid. The base of the probing tip 136 is isolated from the wellbore 114 by an o-ring 140, or other sealing devices (packers).

30 Before completion of a well, the modular dynamics tester is lowered into the well on the wireline 112. After reaching a target depth, i.e., the layer of the formation which is to be sampled (here: 142), the hydraulic arms 134 are extended to engage the sample probe tip 136 with the formation. The o-ring

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140 at the base of the sample probe 136 forms a seal between the side of the wellbore 144 and the formation 142 into which the probe 136 is inserted and prevents the sample probe 136 from acquiring fluid directly from the borehole 114.

Once the sample probe 136 is inserted into the formation 142, an electrical signal is passed down the wireline 112 from the surface so as to start the pump 132 and the sensor systems 116 and 130 to begin sampling of a sample of fluid from the 10 formation 142. The potentiometric detector 116 is adapted to measure the pH and ion-content of the formation effluent.

A bottle (not shown) within the MDT tool may be filled initially with a calibration solution to ensure in-situ (downhole) 15 calibration of sensors. The MDT module may also contain a tank with a greater volume of calibration solution and/or of cleaning solution which may periodically be pumped through the sensor volume for cleaning and re-calibration purposes.

20 Potentiometric probes in an MDT-type downhole tool may be used for the absolute measurements of downhole parameters which significantly differ from those measured in samples on the surface (such as pH, Eh, dissolved H2S, CO2). This correction of surface values are important for water chemistry model validation. 25

A further possible application of the novel sensor and separation system is in the field of measurement-while-drilling (MWD). The principle of MWD measurements is known and disclosed in a vast amount of literature, including for example United States Patent No. 5,445,228, entitled "Method and apparatus for formation sampling during the drilling of a hydrocarbon well".

In FIG. 12, there is shown a wellbore 211 and the lower part of a drill string 212 including the bottom-hole-assembly (BHA) 210. 35

The BHA carries at its apex the drill bit 213. It includes further drill collars that are used to mount additional equipment such as a telemetry sub 214 and a sensor sub 215. The telemetry sub provides a telemetry link to the surface, for example via mud-pulse telemetry. The sensor sub includes the novel potentiometric analyzing unit 216 as described above. The analyzing unit 216 collects fluids from the wellbore via a small recess 217 protected from debris and other particles by a metal mesh.

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During drilling operation wellbore fluid enters the recess 217 and is subsequently analyzed using sensor unit 216. The results are transmitted from the data acquisition unit to the telemetry unit 214, converted into telemetry signals and transmitted to the surface.

A third application is illustrated in FIG. 13. It shows a venturi-type flowmeter 310, as well known in the industry and described for example in the United States Patent No. 5,736,650. Mounted on production tubing or casing 312, the flowmeter is installed at a location within the well 311 with a wired

connection 313 to the surface following known procedures as disclosed for example in the United States Patent No. 5,829,520.

The flowmeter consists essentially of a constriction or throat 314 and two pressure taps 318, 319 located conventionally at the entrance and the position of maximum constriction, respectively. Usually the venturi is combined with a densionmeter 315 located further up- or downstream.

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The novel potentiometric analyzing unit **316** is preferably located downstream from the venturi to take advantage of the mixing effect the venturi has on the flow. A recess **317** protected by a metal mesh provides an inlet to the unit.

During production wellbore fluid enters the recess 317 and is subsequently analyzed using sensor unit 316. The results are transmitted from the data acquisition unit to the surface via wires 313.

The above system allows continuous measurements in a water-inoil emulsion up to 90 vol% of crude oil. An exemplary measurement has been performed in a shut oil producer and is 10 depicted in FIG 14.

The logs #1 and #2 were recorded using a potentiometric probe as described in FIG. 3. The recording took place after pulling out tubing in a cased well (ID casing 139.7 mm) in the Kazanskoe oilfield, Suhodol area, 120 km north-east from Samara city, Russia.

Log#1 was recorded with separated pH and reference electrodes without water-wet connection between the electrodes. No signal 20 was recorded in oil layer (700-870m) due to the absence of an electrical contact. In the underlying brine a stable reproducible signal was recorded. This is due the water-wet surface of a glass pH electrode (no oil fouling) and continuous induced discharge of the reference KCl solution out of the reference electrode (no fouling of the reference junction.

Log#2 was recorded with a capillary contact between the reference electrode and the pH glass membrane ("connector"). KCl solution was continuously pushed out of the reference. This ensured a direct discharge of KCl liquid onto glass membrane, i.e. a stable electrical contact in oil. Note that the presence of the connector resulted in reasonable pH values in a layer of nearly pure oil (700-870 m) (red and blue lines). These values roughly correspond to the pH of brine just below oil layer. Note



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also the good agreement between upwards and downwards logs recorded at different speeds in brine.

The stability of a signal / electrode fouling was checked via 5 measuring a signal with and without an additional resistance as a function of time (see Fig.9).

Design of new electrodes and use of new combinations of potentiometric electrodes in oil-water mixtures

A new gas sensing combination is proposed which allows simultaneous determination of partial pressures of CO₂ and H₂S in any phase (oil, gas, water). This is a modification of existing gas-sensing combinations. The novelty is that the present invention proposes the use of three electrodes (pH, pS, and reference) in one sensor in order to obtain simultaneously the partial pressures for the above two gases.

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CLAIMS

- A wellbore effluent potentiometric sensor comprising at least one reference electrode;
- at least one measuring electrode; and
 at least one connector between said reference and said
 measuring electrode, wherein said electrodes and connector
 form said potentiometric sensor exposed in operation to said
 wellbore effluent via an opening or sample channel and
- wherein said connector provides a continuous conductive path between said reference and said measuring electrode in the presence of hydrocarbon containing effluent.
- A sensor according to claim 1 wherein the connector
 comprises a porous material.
 - 3. A sensor according to claims 1 or 2 wherein the connector comprise an aqueous solution or gel.
- 20 4. A sensor according to claims 1-3 further comprising a discharge element adapted to release an aqueous solution or gel into the connector.
- 5. A sensor according to claim 4 wherein the discharge element is self-discharging in the wellbore.
 - 6. A sensor according to claim 4 wherein the discharge element is controlled by an external control unit.
- 7. Downhole tool for measuring characteristic parameter of wellbore effluent comprising a potentiometric sensor having at least one reference electrode; at least one measuring electrode; and at least one connector between said reference and said measuring electrode, wherein said electrodes and connector

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form said potentiometric sensor exposed in operation to said wellbore effluent via an opening or sample channel and wherein said connector provides a continuous conductive path between said reference and said measuring electrode in the presence of hydrocarbon containing effluent .

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ABSTRACT

A potentiometric sensor for wellbore applications having a

5 permanent aqueous contact between measuring and reference
electrode, whereby contact is ensured by discharging the
internal solution from the reference electrode directly onto a
measuring (ion-sensitive) membrane and protecting the reference
junction of the reference electrode with water wet porous

10 material, such as sintered glass. It is advantageously applied
to oil-water mixtures under high pressure and/or temperature.

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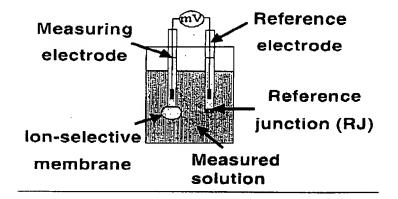


FIG. 1 (Prior Art)

Reference electrode - keeping fixed potential

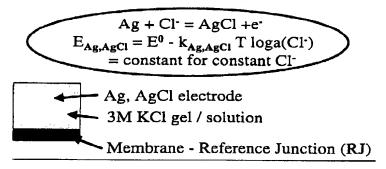


FIG. 2 (Prior Art)

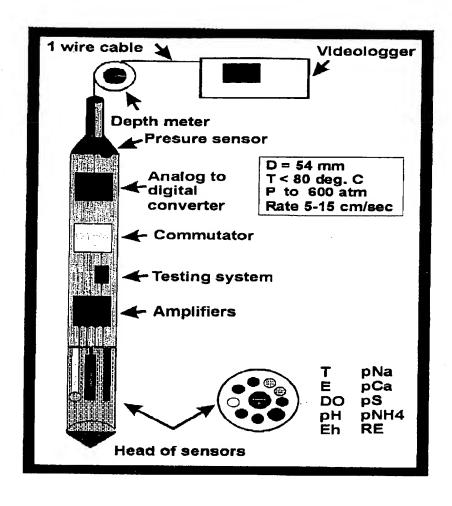
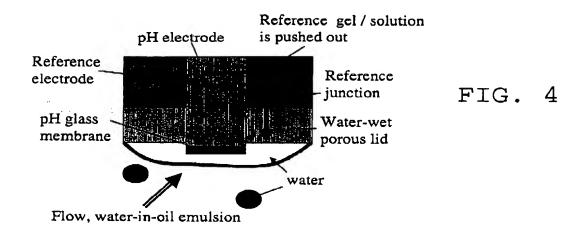


FIG. 3 Prior Art

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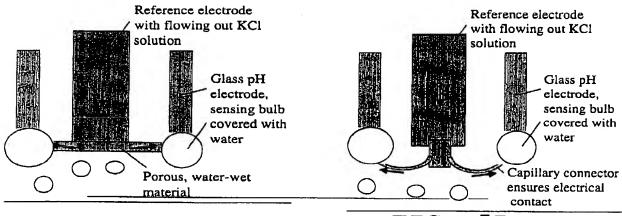


FIG. 5A

FIG. 5B

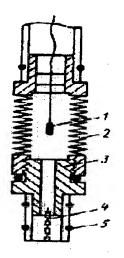


FIG. 6

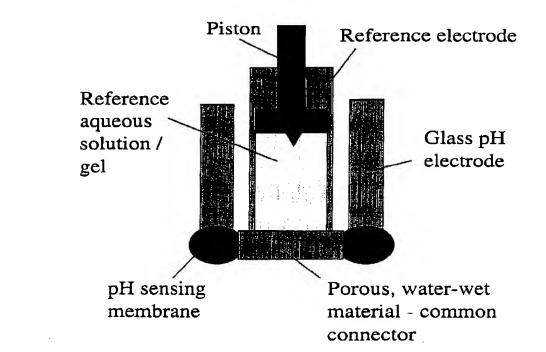
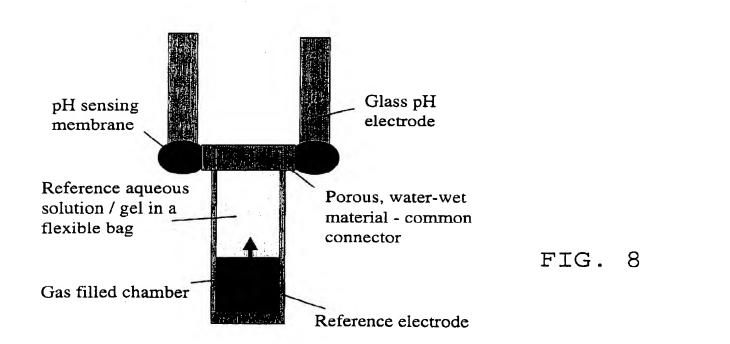


FIG. 7



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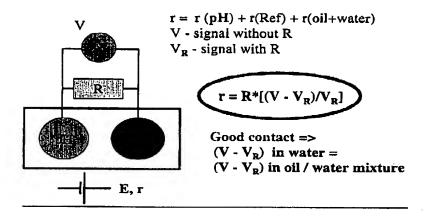


FIG. 9

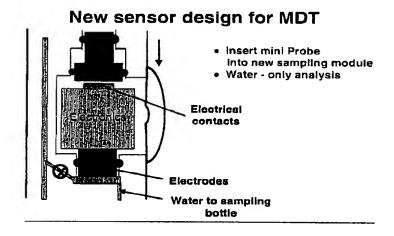
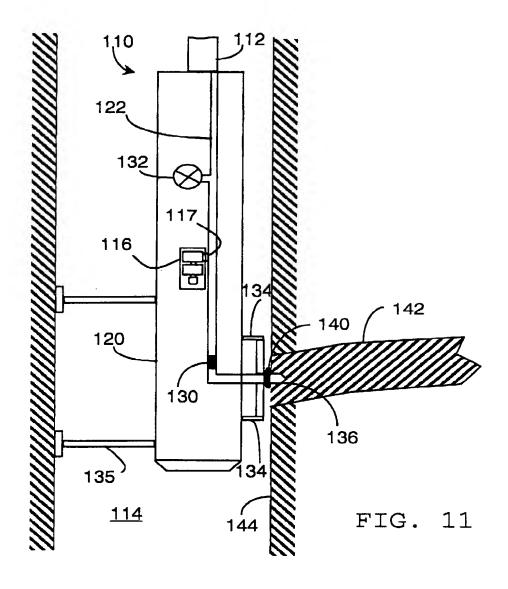
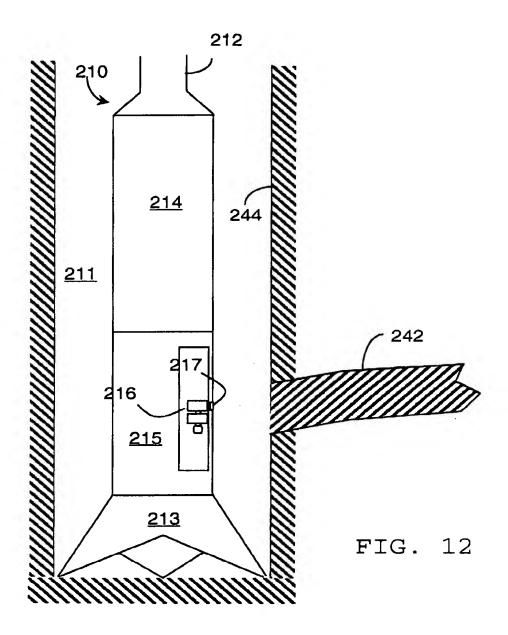
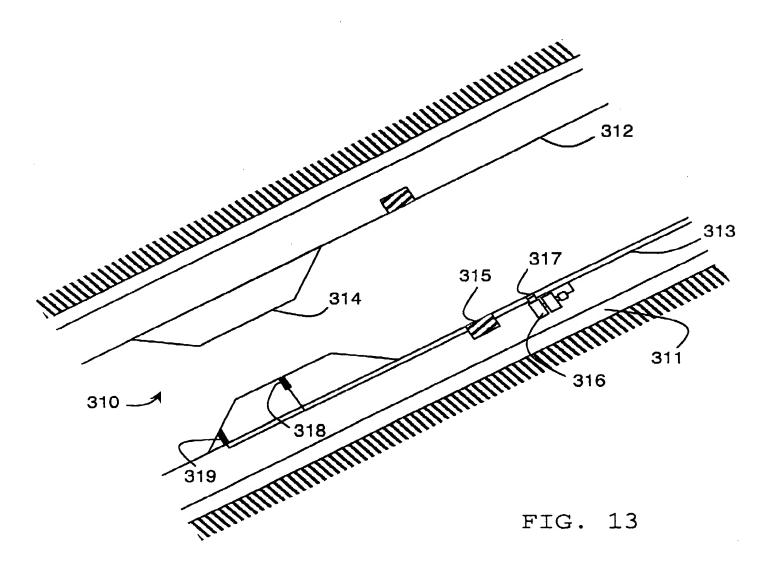


FIG. 10

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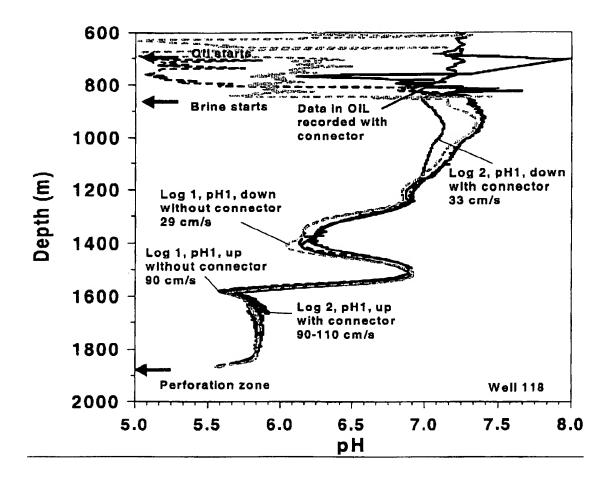


FIG. 14